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Preparation, structure and ferromagnetic properties of the nanocrystalline $Ti_{1-x}Mn_xO_2$ thin films grown by radio frequency magnetron co-sputtering*

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This paper reported that the Mn-doped TiO_2 films were prepared by radio frequency (RF) magnetron co-sputtering. X-ray diffraction measurements indicate that the samples are easy to form the rutile structure, and the sizes of the crystal grains grow big and big as the Mn concentration increases. X-ray photoemission spectroscopy measurements and high resolution transmission electron microscope photographs confirm that the manganese ions have been effectively doped into the TiO_2 crystal when the Mn concentration is lower than 21%. The magnetic property measurements show that the $Ti_{1-x}Mn_xO_2$ ($x = 0.21$) films are ferromagnetic at room temperature, and the saturation magnetization, coercivity, and saturation field are 16.0 emu/cm^3, 167.5×80 A/m and 3740×80 A/m at room temperature, respectively. The room-temperature ferromagnetism of the films can be attributed to the new rutile $Ti_{1-x}Mn_xO_2$ structure formed by the substitution of Mn^{4+} for Ti^{4+} into the TiO_2 crystal lattice, and could be explained by O vacancy (V_O)-enhanced ferromagnetism model.

Keywords: RF magnetron sputtering, Mn-doped TiO_2 films, room-temperature ferromagnetic properties

PACC: 8115C, 6170T, 7500, 7550P

1. Introduction

As one of the important wide band gap ($E_g > 3$ eV) semiconductor oxides, titanium dioxide has been extensively applied for photo-voltaic, solar cells, photo catalysts, protective coatings and gas sensors. Recent discovery of ferromagnetism above room temperature in 3d transition metal-doped TiO_2 as possible diluted magnetic semiconductors (DMSs) for magneto-electronic applications[1−4] has been drawing more and more researchers' increasing attention on transparent ferromagnetic semiconductors. For example, ZnO[5−8] and TiO_2[9−11] doped by Fe[12], Co[13], V[14], Cr[15] and other magnetic elements have been prepared by PLD[16], MBE[17], magnetron sputtering[12] and other methods. However, only a few research reports on Mn doped to TiO_2 could be found.[18,19] This paper deals with the structural and ferromagnetic properties of the nanocrystalline $Ti_{1-x}Mn_xO_2$ thin films grown on glass by radio frequency magnetron co-sputtering. The effects on the structural properties of Mn doping TiO_2 films have been investigated by using x-ray diffraction (XRD), scanning electron microscope (SEM) and high resolution transmission electron microscope (HRTEM). The chemical states of the TiO_2 films have also been investigated by x-ray photoemission spectra (XPS). And the effects on the ferromagnetic properties of Mn doping TiO_2 films have been studied by using a vibrating sample magnetometer (VSM).

2. Experiment

The $Ti_{1-x}Mn_xO_2$ thin films were deposited by radio frequency magnetron co-sputtering. A TiO_2 ceramic plate, 60 mm in diameter and 3 mm in thickness, was used as target, on which some pieces of high

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purity (99.98%) Mn chips were attached in order to vary the Mn concentration doped in TiO_2 films. Glass substrates (20 mm × 20 mm × 0.8 mm) were ultrasonically washed successively in acetone, alcohol and deionized water to obtain a clean surface before they were placed in a vacuum chamber. When the chamber was evacuated to a pressure of 1×10^{-4} Pa, high purity (99.9999%) argon gas was introduced. The sputtering power was set to 80 W. During sputtering, the chamber pressure was maintained at 2 Pa. At the same time, the film was heated by the coil of electric resistance in situ at 500°C. In order to make sure that the parameters were stable and the surface of the target was clean enough, the sputtering began 10 minutes before the substrate was moved above the target.

The $Ti_{1-x}Mn_xO_2$ films were characterized by XRD, SEM, HRTEM and XPS, and the magnetic properties was measured by using a VSM. XRD studies were carried out on an X'Pert Pro XRD system with x-ray Mirror PFX and with an operating voltage of 40 kV and a current of 40 mA. The microshape of the sample surface and the concentration of Mn content were measured on a FEI-SIRION SEM. The transmission electron microscope (TEM) micrographs were obtained on PHILIPS-CM200 and JEM-2010 type TEMs. The XPS measurements were accomplished with a VG-ESCALAB-MKII spectrometer by using an Al Kα x-ray source with the analyser mode set at a constant energy of 50 eV. The x-ray source was run at 120 W and a takeoff angle of 80°. All the peak energies in the spectra were referenced with respect to the C1s peak (284.6 eV). The magnetic properties of the films were measured on a Lake Shore-VSM7404 VSM at room temperature.

3. Results and discussion

Figure 1(a) shows the XRD patterns of $Ti_{1-x}Mn_xO_2$ films with various Mn concentrations. The XRD results show that the films are single-phase reduced-rutile, with good crystallization. The average diameters of the grains in the films with Mn concentration $x = 0.10$, 0.21, 0.23 are calculated to be 7.53 nm, 13.20 nm, 17.62 nm, respectively.

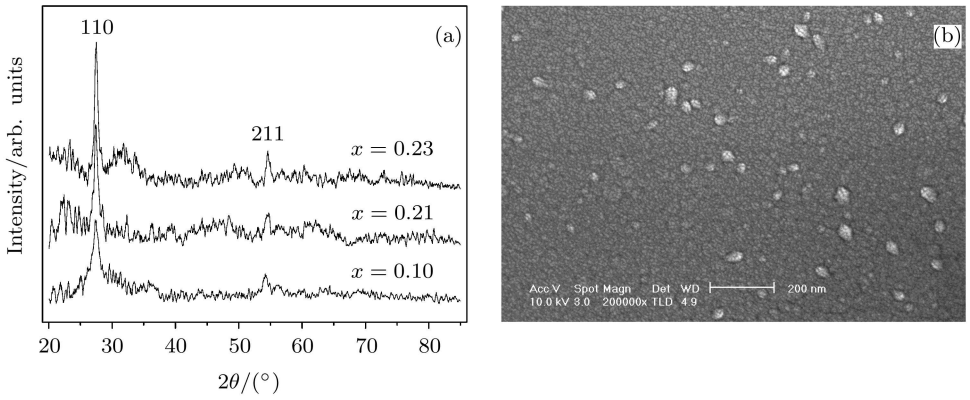


Fig.1. XRD patterns and SEM image of the films. (a) XRD patterns of $Ti_{1-x}Mn_xO_2$ films with various Mn concentrations. (b) SEM image for $Ti_{1-x}Mn_xO_2$ film ($x = 0.21$).

It can be seen that the grains in the films become big and big as the Mn concentrations increase, which due to that the Mn ions doped TiO_2 are easy to form the rutile crystals.[20] It is interesting to note that there are no peaks of other phases. So it can be concluded that the Mn ions have already been doped into the crystal of rutile TiO_2, but no Mn clusters or any other Mn-Ti-O structures formed.

Figure 1(b) shows the SEM image for $Ti_{1-x}Mn_xO_2$ film. It shows the good nanocrystalline $Ti_{1-x}Mn_xO_2$ formed, and this image suggests that the film is uniform. The section image of TEM for $Ti_{1-x}Mn_xO_2$ film is shown in Fig.2(a). One can see that the thickness of the film is about 200 nm, and can certainly affirm that the film is uniform.

Figure 2(b) shows the HRTEM image of a $Ti_{1-x}Mn_xO_2$ ($x = 0.21$) film. It is also interesting to note that there is no impurity phases observed in the film. The spacing of parallel atomic planes, 0.318 nm, is marked on Fig.2(b), and is consistent with the interplanar distance of (110) crystal planes of rutile TiO_2. Therefore, it is concluded that the rutile $Ti_{1-x}Mn_xO_2$ crystals are synthesized by substitution of Mn^{4+} for Ti^{4+}.

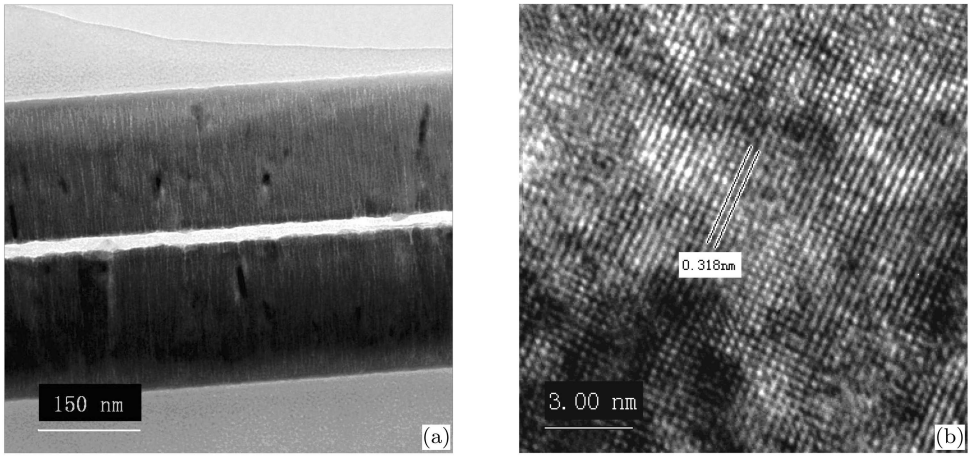


Fig.2. TEM images of a $Ti_{1-x}Mn_xO_2$ ($x = 0.21$) film. (a) The section of TEM image for $Ti_{1-x}Mn_xO_2$ films ($x = 0.21$). (b) High resolution TEM image of a $Ti_{1-x}Mn_xO_2$ ($x = 0.21$) film.

Figure 3(a) shows the XPS of $Ti_{1-x}Mn_xO_2$ film. It can be seen that there are Ti, O, and Mn in the films. All the element banding energies in the spectra were referenced with respect to the C1s peak (284.6 eV).

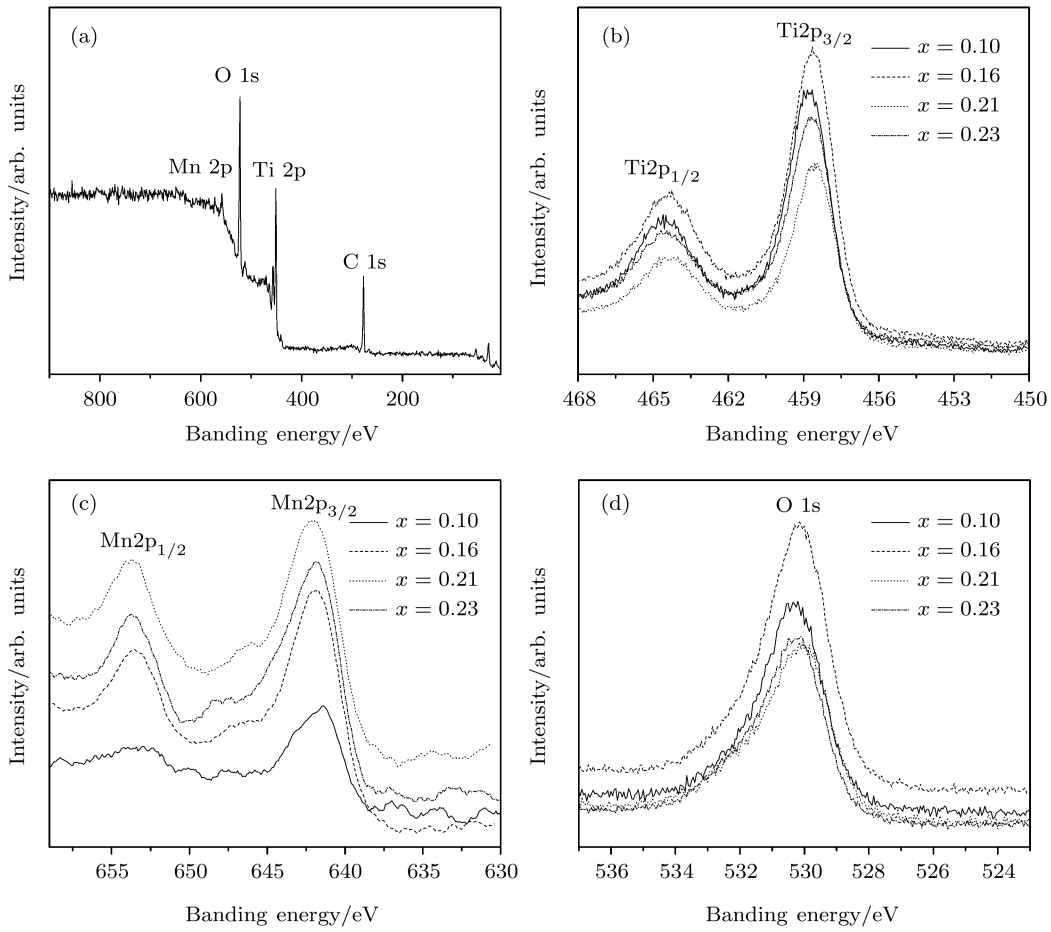


Fig.3. XPS of $Ti_{1-x}Mn_xO_2$ films. (a) XPS of $Ti_{1-x}Mn_xO_2$ film. (b)–(d) Ti 2p, Mn 2p, and O 1s core levels of the $Ti_{1-x}Mn_xO_2$ films with various Mn concentrations.

Figure 3(b) and Table1 together indicate XPS Ti 2p core level and peak separation of the $Ti_{1-x}Mn_xO_2$ films with various Mn concentrations. The peak separation is around 5.7 eV, which indicates that Ti in the films is assigned to the Ti^{4+} (TiO_2).[21] As the Mn concentration increases the core level of Ti 2p decreases a little, but when the Mn concentration gets a level of 23%, it enhances a bit. The origin is because the radius of Mn^{4+} is smaller than that of Ti^{4+}; the substitution of Mn^{4+} for Ti^{4+} will pull the adjacent O^{2-} ions to themselves. As a result, the bonding between O^{2-} and Ti^{4+} becomes weaker, and the core level of Ti 2p decreases a little as the Mn concentration increases. Also when the Mn concentration gets a certain level, the redundant Mn and some other Mn could get together to form a certain structure, the core level of Ti 2p turns to a bit high when the Mn concentration gets above a level of 23%.

Table 1. XPS Ti 2p core level and peak separation of the $Ti_{1-x}Mn_xO_2$ films with various Mn concentrations.

Mn content x	Ti $2p_{1/2}$	Ti $2p_{3/2}$	separation between two peaks
0.10	464.55	458.80	5.75
0.16	464.35	458.65	5.70
0.21	464.30	458.55	5.75
0.23	464.45	458.70	5.75

Figure 3(c) and Table 2 together indicate XPS Mn 2p core level and peak separation of the $Ti_{1-x}Mn_xO_2$ films with various Mn concentrations. The separation between two peaks is around 11.6 eV. This indicates that the Mn in the films is assigned to the Mn^{4+} ions,[21,22] which replace the Ti^{4+} and become a new crystal of the $Ti_{1-x}Mn_xO_2$. As the Mn concentration increases, the core level of Mn 2p enhances a little (about 0.2–0.7 eV), but when the Mn concentration gets a level of 23%, it decreases a bit by 0.3 eV. When the Mn concentration is not so high enough to destroy the rutile structure, some Mn^{4+} ions substitute for Ti^{4+} ions sites and the core level of Mn 2p becomes higher than that of pure TiO_2. But when the Mn concentration gets a critical value, the redundant Mn could get together to form another structure in which Mn is in its low valence. So the Mn 2p core levels become a little low and the peak separation is bigger than that of the pure TiO_2.

Figure 3(d) and Table 3 together indicate XPS O1s core level of $Ti_{1-x}Mn_xO_2$ films with various Mn concentrations. Consistent with Ti, as the Mn concentration increases the core level of O 1s decreases a little, but when the Mn concentration gets a level of 23%, it turns to a bit high.

Table 2. XPS Mn 2p core level and peak separation of the $Ti_{1-x}Mn_xO_2$ films with various Mn concentrations.

Mn content x	Mn $2p_{1/2}$	Mn $2p_{3/2}$	Separation between two peaks
0.10	653.0	641.4	11.6
0.16	653.5	641.9	11.6
0.21	653.7	642.1	11.6
0.23	653.8	641.8	12.0

Table 3. XPS O 1s core level of $Ti_{1-x}Mn_xO_2$ films with various Mn concentrations.

Mn content x	O 1s
0.10	530.35
0.16	530.15
0.21	530.05
0.23	530.25

Figure 4 shows the hysteresis loops for $Ti_{1-x}Mn_xO_2$ ($x = 0.21$, 0.23) films in magnetic field parallel to the film plane, which was measured on a Lake Shore-VSM 7404 VSM at room temperature. It is found that the saturation magnetization, coercivity, and saturation field are 16.0 emu/cm^3, 167.5×80 A/m and 3740×80 A/m at room temperature, respectively.

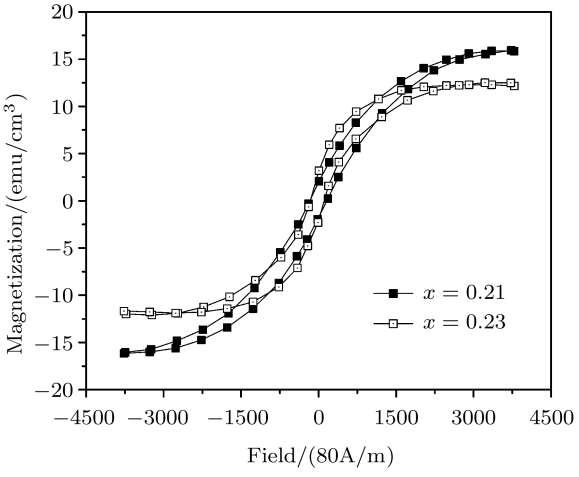


Fig.4. The hysteresis loops for $Ti_{1-x}Mn_xO_2$ ($x = 0.21$, 0.23) films in magnetic field parallel to the film plane, which was measured on a Lake Shore-VSM 7404 VSM at room temperature.

It is observed by both XRD and XPS that there is no Mn metal phase in the films. Furthermore, Mn and Mn oxides, including Ti/Mn oxides, are not ferromagnetic except Mn_3O_4 and perhaps certain Mn–Ti.[23,24] But the latter two have Curie temperatures

in the 40 K range, too low to account for the room temperature ferromagnetism. Mn, MnO, Mn_2O_3, MnO_2, and $MnTiO_3$ are antiferromagnetic. So the room-temperature ferromagnetism of the films contributed to the new structure formed by the substitution of the Mn^{4+} for Ti^{4+} and finally rutile crystals of the $Ti_{1-x}Mn_xO_2$. Although the room temperature ferromagnetism in the sample is not understood, it is expected to share the same origin as that of Fe-doped rutile TiO_2,[25] which have O vacancy (V_O)-enhanced ferromagnetism.

When the Mn concentration is 23%, the film was observed to be a little antiferromagnetic. According to the XPS measurement, the antiferromagnetism is properly due to the low valance Mn oxides in the film. But the Mn oxides are so few that they are not present in the XRD pattern. And the decrease of the magnetic moment at high Mn concentration ($x = 0.23$) is possibly due to the increased antiferromagnetic superexchange interaction between Mn moments which, in general, leads to a spin-glass-like state as observed in many II–VI dilute magnetic semiconductors above 20% Mn.[26,27]

4. Conclusions

The $Ti_{1-x}Mn_xO_2$ ($x = 0.10, 0.16, 0.21, 0.23$) thin films have been successfully grown by RF magnetron co-sputtering. The samples are easy to form the rutile TiO_2 structures and the sizes of the crystal grains grow big and big as the Mn concentration increases. The Mn^{4+} has been effectively doped into the TiO_2 crystal when the Mn concentration is lower than 21%. The $Ti_{1-x}Mn_xO_2$ ($x = 0.21$) thin film has ferromagnetic properties at room temperature, and the saturation magnetization, coercivity, and saturation field are 16.0 emu/cm^3, 167.5×80 A/m and 3740×80 A/m at room temperature, respectively. The mechanism of room-temperature ferromagnetic properties of the $Ti_{1-x}Mn_xO_2$ film was originated in the new structure of rutile $Ti_{1-x}Mn_xO_2$ crystals formed by the substitution of Mn^{4+} for Ti^{4+}. But when the Mn concentration gets to a level of 23%, low valance Mn oxides will appear in the film.

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